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(54) A thermoplastic resin-based molding composition.

(57) The thermoplastic polymeric molding composition of the invention has good moldability in shaping by injection molding, extrusion molding and compression molding and capable of giving shaped articles having good machinability in mechanical working such as cutting, grinding and lathing. The composition is compounded from 2 to 70 parts by weight of a thermoplastic polymer such as a polyamide resin and from 98 to 30 parts by weight of a metallic filler such as zinc powder and zinc oxide powder having a surface coated with a water repellent agent such as silane coupling agents, titanate coupling agents and silicone fluids in a specified amount. A part of the above mentioned particulate filler may optionally be replaced with a fibrous filler such as glass fibers and carbon fibers so that the shaped articles of the molding composition may be imparted with increased impact strength.

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A THERMOPLASTIC RESIN-BASED MOLDING COMPOSITION

BACKGROUND OF THE INVENTION

The present invention relates to a thermoplastic resin-based molding composition or, more particularly, to a molding composition based on a thermoplastic resin as the matrix compounded with a specific filler and suitable for molding various shaped articles used in a wide variety of applications including, for example, structural parts in electric and electronic instruments, industrial machines and transportation machines such as automobiles as well as furnitures and other household commodities.

As is well known, thermoplastic resins have advantages over metallic materials in repsect of their good workability, excellent corrosion resistance, lightness in weight and inexpensiveness so that they are useful as a base material for the manufacture of various shaped articles such as structural parts of instruments and machines as well as furnitures and other household commodities.

Thermoplastic resins in general, however, are inferior in the mechanical properties such as tensile strength, impact strength and hardness in comparison with metallic materials and are not quite satisfactory in respect of the heat resistance and dimensional stability. Moreover, the usually advantageous feature of lightness in weight may in some cases cause a disadvantage to give a trifling impression as commercial goods.

A proposal has been made to solve the above described problems by compounding a thermoplastic resin with a metallic filler. For example, thermoplastic resins such as polypropylene, polyethylene, polyamide, poly(ethylene terephthalate), poly(butylene terephthalate) and the like are compounded with a fine powder of a metal such as zinc, copper, iron and the like as a filler to give a resin-based composite molding compound.

Shaped articles prepared from such a metal-filled molding compound, however, more or less have an unavoidable serious problem of rusting of the metal particles contained in the shaped article to cause poor appearance or degradation in the mechanical properties when the article is prolongedly kept in humid air, water, soil or other corrosive environment. When rusting occurs in the molding compound before molding, which is usually in the form of pellets, moreover, drawbacks, are sometimes caused in the molding work of such a deteriolated molding compound.

Several methods have been proposed to solve this problem including a method of forming a corrosion-resistant coating layer of, for example, a rust inhibitor, metal plating and ceramic on the surface of the shaped article, a method of forming a relatively thick uniform skin layer of a rust-free resin on the surface of the shaped article and a method of wrapping the shaped article with a film of a plastic resin having a small permeability to moisture.

These methods, however, cannot provide a complete solution of the problem. For example, the corrosion-resistant coating layer formed on the surface of a shaped article has a problem of inherently low durability because the coating layer gradually falls off the surface in the lapse of time. In addition, the productivity of shaped articles must decrease because the process is complicate for forming such a protective surface layer. The method of forming a skin layer is particularly defective when the shaped article has an irregular configuration or non-uniform wall thickness due to the extreme difficulty in obtaining a skin layer of uniform thickness. The productivity of course cannot be high enough. The method of wrapping with a plastic film also suffers low productivity due to the complicate and troublesome process if not to mention the limited applicability of the method.

In addition to the above described problem due to rusting of metal particles, conventional metallic filler-loaded composite molding compounds have problems in the moldability of the compound and stability of the shaped articles therefrom, especially, when the molding compound has a density in excess of 1.5 g/cm^3 or, in particular, 2.0 g/cm^3. The moldability of such a molding compound is poor so that the appearance of the articles shaped therefrom is sometimes not quite acceptable. Moreover, the shaped articles of such a molding compound usually have relatively low mechanical strengths or, in particular, impact strength and exhibit a large molding shrinkage sometimes with different ratios of shrinkage between directions. Therefore, it is a rather difficult matter to obtain a satisfactory shaped article of high density with good dimensional stability exhibiting no warping distortion from such a metallic filler-loaded molding compound.

Further, degradation of the matrix resin may sometimes take place in such a metallic filler-loaded composite molding compound due to the influence of the metal particles. The molding compound is also not quite satisfactory as a moldable electroconductive material because sufficiently high electroconductivity can hardly be obtained or the repro ducibility of the conductivity, if obtained, is usually low.

SUMMARY OF THE INVENTION

An object of the present invention therefore is to provide a noveal thermoplastic resin-based molding composition loaded with a metallic filler free from the above described problems and disadvantages in the conventional metallic filler-loaded molding compounds. Namely, the molding composition of the present invention should have good moldability and be capable of giving shaped articles having good appearance and high mechanical properties as well as dimensional stability, electroconductivity and resistance against rusting and also suitable for secondary machining such as cutting, grinding and lathing using standard machine tools.

As a result of the extensive investigations undertaken with the above mentioned object, it has been unexpectedly discovered that the problems can be solved by compounding a thermoplastic resin with a specific amount of a metallic filler after a surface treatment of the particles with a specific amount of a compound belonging to the class of so-called water repellent agents, optionally, with further admixture of a small amount of a low-molecular oxidized poly propylene.

Thus, the thermoplastic resin-based molding composition of the present invention comprises:

(A) from 2 to 70 parts by weight of a thermoplastic polymer as the matrix phase; and

(B) from 98 to 30 parts by weight of a metallic filler, of which the particles have a surface coated with a water repellent agent, the amount of the water repellent agent being in the range from 0.01 to 5% or, preferably, from 0.3 to 3% by weight by weight based on the metallic filler before coating therewith.

When the molding composition is additionally admixed with (C) a low-molecular oxidized polypropylene, the composition comprises:

(A) from 2 to 70 parts by weight of a thermoplastic polymer;

(B) from 98 to 30 parts by weight of a metallic filler, of which the particles have a surface coated with a water repellent agent, the amount of the water repellent agent being as mentioned above; and

(C) a low-molecular oxidized polypropylene in an amount in the range from 0.1 to 2% by weight based on the total amount of the components (A) and (B).

Although the above mentioned metallic filler is usually in a particulate form, it is sometimes advantageous that a part of such a particulate filler is replaced with a fibrous filler. Namely, the metallic filler as the component (B) in the above given formulations should be a combination of a particulate metallic filler having an average particle diameter, for example, in the range from 0.1 to 20 μm and a fibrous metallic filler having a fiber diameter in the range from 0.03 to 60 μm or, preferably, from 0.1 ~ 20 μm and an aspect ratio in the range from 50 to 2500 in a weight ratio not exceeding 1:1 or, preferably, in the range from 1:1 to 30:1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The component (A) to form the matrix phase of the inventive molding composition is a thermoplastic polymer which is not limited to a particular type but may be selected from various kinds of thermoplastic resins and elastomers either singly or as a combination of two kinds or more according to need.

The above mentioned thermoplastic resins include polyolefin resins, poly(vinyl chloride) resins, polyamide resins, polyimide resins, polyester resins, polyacetal resins, polycarbonate resins, poly(aromatic ether or thio ether) resins, poly(aromatic ester) resins, polysulfone resins, polystyrene resins, acrylic resins, fluorocarbon resins and the like.

The polyolefin resins include homopolymers and copolymers of α-olefins such as ethylene, propylene, butene-1, 1-methyl-butene-1, 3-methylpentene-1, 4-methylpentene-1 and the like as well as copolymers of these monomers as the principal ingredient with another monomer of a different type. Typical examples of the polyolefin resins are high-density, medium-density and low-density polyethylenes, straight-chained polyethylenes, super-high molecular polyethylenes, copolymers of ethylene and vinyl acetate and other ethylene-based polymers, atactic, syndiotactic and isotactic polypropylenes, block and random copolymers of propylene and ethylene and other propylene-based polymers, poly(4-methylpentene-1) and the like.

Further, these polyolefins may be modified by the graft polymerization of a polar vinylic monomer such as α,β-unsaturated carboxylic acids and esters thereof exemplified by acrylic acid, esters of acrylic acid, methacrylic acid, esters of methacrylic acid, maleic acid, fumaric acid, citraconic acid, itaconic acid, crotonic acid and the like or an unsaturated epoxide exemplified by glycidyl acrylate, glycidyl methacrylate, vinyl glycidyl ether, allyl glycidyl ether and the like.

The poly(vinyl chloride) resins include homopolymeric poly(vinyl chloride) resins and copolymeric resins of vinyl chloride with another monomer copolymerizable therewith. The copolymeric resins are exemplified by the copolymers of vinyl chloride and an acrylic acid ester, copolymers of vinyl chloride and a methacrylic acid ester, copolymers of vinyl chloride and ethylene, copolymers of vinyl chloride and propylene, copolymers of vinyl chloride and vinyl acetate, copolymers of vinyl chloride and vinylidene chloride and the like. These poly(vinyl chloride) resins may be post-chlorinated to have an increased content of chlorine.

The polyamide resins include 6-nylon, 12-nylon and the like obtained by the ring-opening polymerization of an aliphatic cyclic lactam, 6,6-nylon, 6,10-nylon, 6,12-nylon and the like obtained by the condensation-polymerization of an aliphatic diamine and an aliphatic dicarboxylic acid, condensation-polymerizate of m-xylene and adipic acid and the like obtained by the condensation-polymerization of an aromatic diamine and an aliphatic dicarboxylic acid, condensation-polymerizates of p-phenylene diamine and terephthalic acid or m-phenylene diamine and isophthalic acid and the like obtained by the condensation-polymerization of an aromatic diamine and an aromatic dicarboxylic acid, 11-nylon and the like obtained by the condensation-polymerization of an amino acid, and so on.

The polyimide resins include polyimides and polyamideimides. Exemplary of the polyimides are those obtained from the combinations of pyromellitic anhydride and diamino diphenyl ether, 3,4,3′,4′-benzophenone tetracarboxylic acid anhydride and diamino diphenyl ether, bismaleimide and diamino diphenyl methane and the like. Exemplary of the polyamideimides are those obtained from the combination of trimellitic anhydride and diamino diphenyl ether and the like.

The polyester resins include those obtained by the condensation-polymerization of an aromatic dicarboxylic acid and an alkylene glycol exemplified by poly (ethylene terephthalates), poly (methylene terephthalates) and the like.

The polyacetal resins are exemplified by the homopolymeric polyoxymethylenes and copolymers of formaldehyde and ethylene oxide obtained from trioxane and ethylene oxide.

Preferable examples of the polycarbonate resins are the 4,4′-dihydroxy diallyl alkane-based polycarbonates and the bisphenol A-based polycarbonates prepared by the phosgene method, in which bisphenol A and phosgene are reacted, or the ester interchange method, in which bisphenol A and a diester of carbonic acid such as diphenyl carbonate are reacted. Usable polycarbonate resins include those modified or flame-retardant bisphenol A-based polycarbonates obtained by partially replacing the bisphenol A in the above mentioned preparation of unmodified polycarbonates with 2,2-bis(4-hydroxy-3,5-dimethyl phenyl) propane, 2,2-bis(4-hydroxy-3,5-dibromo phenyl) propane and the like.

The poly(aromatic ether or thioether) resins have ether linkages or thioether linkages in the polymeric molecular chain and are exemplified by polyphenylene oxides, styrene-grafted polyphenylene oxides, polyphenylene sulfides and the like.

The poly(aromatic ester) resins are exemplified by polyoxybenzoyls obtained by the condensation-polymerization of 4-hydroxy benzoic acid and polyarylates obtained by the condensation-polymerization of bisphenol A and an aromatic dicarboxylic acid such as terephthalic acid and isophthalic acid.

The polysulfone resins have sulfone linkages in the polymeric molecular chain and are exemplified by polysulfones obtained by the condensation-polymerization of bisphenol A 4,4′-dichlorodiphenyl sulfone, polyether sulfones having a structure in which phenylene groups are bonded together at the 1,4-positions through ether linkages and sulfone linkages and polyaryl sulfones having a structure in which diphenylene groups and diphenylene ether groups are alternately bonded together through sulfone linkages.

The polystyrene resins include homopolymers of styrene and α-methyl styrene and copolymers thereof as well as copolymers of them as the principal ingredient with another monomer copolymerizable therewith. Typical examples of the polystyrene resins are general-purpose polystyrenes, high-impact polystyrenes, heat-resistant polystyrenes, polymers of α-methyl styrene, copolymers of acrylonitrile, butadiene and styrene (ABS), copolymers of acrylonitrile and styrene (AS), copolymers of acrylonitrile, chlorinated polyethylene and styrene (ACS), copolymers of acrylonitrile, ethylenepropylene rubber and styrene (AES), copolymers of acrylic rubber, acrylonitrile and styrene and the like.

The acrylic resins include polymers of acrylic acid esters and methacrylic acid esters exemplified by methyl, ethyl, n-propyl, isopropyl and butyl esters of acrylic acid and methacrylic acid. Particularly preferable among them are poly(methyl methacrylate) resins from the standpoint of practically using the inventive molding composition as an industrial material.

The fluorocarbon resins include homopolymers of tetrafluoro ethylene, hexafluoro propylene, vinylidene fluoride, vinyl fluoride and the like and copolymers thereof as well as copolymers of these fluorinated monomers as the principal ingredient with another monomer copolymerizable therewith. Exemplary of the fluorocarbon resins are poly(tetrafluoroethylenes), poly(vinylidene fluorides), poly(vinyl fluorides), copolymers of tetrafluoroethylene and ethylene, copolymers of tetrafluoroethylene and vinylidene fluoride, copolymers of hexafluorpropylene and vinylidene fluoride, copolymers of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride and the like.

The elastomeric polymers suitable as the component (A) include natural rubber and various kinds of synthetic rubbers exemplified by polybutadiene rubbers (BR), copolymeric rubbers of styrene and butadiene (SBR), copolymeric rubbers of acrylonitrile and butadiene (NBR), copolymeric rubbers of styrene, butadiene and acrylonitrile, polychloroprene rubbers (CR) and other butadiene-based rubbers, polyisoprene rubbers or synthetic natural rubbers, copolymeric rubbers of isobutylene and isoprene or so-called butyl rubbers (IIR), copolymeric rubbers of acrylonitrile and isoprene, polyisobutylene rubbers, copolymeric rubbers of ethylene and propylene, copolymeric rubbers of ethylene and vinyl acetate, chlorinated polyethylenes, chlorosulfonated polyethylenes, urethane rubbers, silicone rubbers, fluorocarbon rubbers, acrylic rubbers, epichlorohydrin rubbers, propylene oxide rubbers, polyester-based elastomers, polyacrylate-based elastomers, polyolefin-based elastomers, poly(vinyl chloride)-based elastomers, copolymeric elastomers of styrene and butadiene, polystyrene-based elastomers, polyamide-based elastomers, polyurethane-based elastomers and the like.

The above named polymers can be used either singly or as a mixture of two kinds or more according to need as the component (A) to form the matrix phase of the inventive molding composition. Particularly preferable among them are polyamide resins such as 6-nylon, 6,6-nylon, 12-nylon and the like, polypropylenes and poly(butylene terephthalates).

The component (B) to form the disperse phase in the inventive molding composition is a metallic filler usually in a particulate form. Metals of which the powder as the metallic filler is prepared include zinc, copper, iron, lead, aluminum, nickel, chromium, titanium, manganese, tin, platinum, tungsten, gold, magnesium, cobalt, strontium and the like as well as alloys of these metallic elements such as stainless steel, solder alloys, brass, bronze and the like, of which zinc is particularly preferred. Zinc oxide also can be used. Certain ceramic materials obtained in a powdery form can be used as the filler including silicon carbide, silicon nitride, zirconia, aluminium nitride, titanium carbide and the like.

The metallic filler in a particulate form as the component (B) should have an average particle diameter in the range from 0.2 to 20 µm or, preferably, in the range from 0.4 to 10 µm. When the filler particles are too fine, the molding composition compounded with the filler may be poor in the moldability. When the filler particles are too coarse, on the other hand, the molding composition compounded with the filler cannot give a shaped article having a sufficiently high impact strength and free from the drawbacks of warping distortion after molding.

When a particularly high impact strength is desired of the shaped article of the inventive molding composition, it is advantageous to replace a part of the above described filler in a particulate form with a fibrous filler. Suitable fibrous fillers include inorganic fibers such as glass fibers, carbon fibers, magnesium sulfate fibers and the like, fibers and whiskers of a metal such as stainless steel, brass, aluminum, nickel and the like, whiskers of ceramics such as potassium titanate, silicon carbide and the like, and organic fibers such as aromatic polyamide fibers, cellulosic fibers, nylon fibers, polyester fibers, polypropylene fibers and the like. Preferable among them are glass fibers, carbon fibers, stainless steel fibers, brass fibers, potassium titanate whiskers, aromatic polyamide fibers and the like. Glass fibers are particularly preferred. These fibrous fibers can be used either singly or as a combination of two kinds or more according to need.

The fibers of the fibrous filler should have a fiber diameter in the range from 0.03 to 60 µm or, preferably, from 0.1 ~ 20 µm and an aspect ratio in the range from 50 to 2500 or, preferably, from 100 to 2000. When the aspect ratio of the fibers is too small, desired improvement in the impact strength of the shaped article cannot be achieved as desired. When the aspect ratio of the fibers is too large, on the other hand, the shaped articles of the molding composition may be subject to an increased molding shrinkage and drawbacks of warping distortion after molding so that the molding composition cannot be used industrially due to the poor dimensional stability of the shaped articles therefrom.

When a particulate filler and a fibrous filler are used in combination as the component (B) in the inventive molding composition, the weight ratio of them should not exceed 1:1 although no substantial improvement can be obtained in the impact strength of the shaped articles molded of the composition when the amount of the fibrous filler is too small. In this regard, the weight ratio of the particulate to fibrous fillers should be in the range from 1:1 to 30:1 or, preferably, from 2:1 to 20:1.

When the inventive molding composition is prepared by compounding the thermoplastic polymer as the component (A) with the filler as the component (B), it is essential that the filler is subjected in advance to a suface treatment with a water repellent agent in a specific amount. Suitable water repellent agents include silane-based coupling agents, titanate-based coupling agents, silicone fluids, higher fatty acids, higher alcohols, waxes and the like, of which silane-based coupling agents, titanate-based coupling agents and silicone fluids are preferred. These water repellent agents can be used either singly or as a combination of two kinds or more according to need.

The type of the above mentioned silane-based coupling agent is not particularly limitative, and any of known ones can be used. Exemplary of suitable silane-based coupling agents are thriethoxy silane, vinyl tris(β-methoxyethoxy) silane, 3-methacryloxypropyl trimethoxy silane, 3-glycdyloxypropyl trimethoxy slilane, 2-(3,4-epoxycyclohexyl)ethyl trimethoxy silane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxy silane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxy silane, 3-aminopropyl triethoxy silane, N-phenyl-3-aminopropyl trimethoxy silane, 3-mercaptopropyl trimethoxy silane, 3-chloropropyl trimethoxy silane and the like, of which 3-aminopropyl triethoxy silane and N-(2-aminoethyl)-3-aminopropyl trimethoxy silane are preferred.

The type of the above mentioned titanate-based coupling agents is also not particularly limitative and any of hitherto known ones can be used. Exemplary of suitable titanate-based coupling agents are isopropyl triisostearoyl titanate, isopropyl tri(dodecylbenzene sulfonyl) titanate, isopropyl tris(dioctyl pyrophosphato) titanate, tetraiso propyl bis(dioctylphosphito) titanate, tetraoctyl bis(ditridecyl phosphito) titanate, tetra(2,2-diallyloxy methyl-1-butyl) bis(di-tridecyl phosphito) titanate, bis(dioctyl pyrophosphato) oxyacetate titanate, bis(dioctyl pyrophosphato) ethylene titanate, isopropyl trioctanoyl titanate, isopropyl dimethacryl isostearoyl titanate, isopropyl tri(dioctyl phosphato) titanate, isopropyl tri(cumyl phenyl) titanate, isopropyl tri(N-amidoethyl aminoethyl) titanate, dicumyl phenyl oxyacetate titanate, di(isostearoyl) ethylene titanate and the like, of which isopropyl triisostearoyl titanate and isopropyl tri(N-amidoethyl amioethyl) titanate are preferred.

Further, suitable silicone fluids include dimethyl silicone fluids, methyl phenyl silicone fluids, polyether-modified silicone fluids, alkyl-modified silicone fluids, methyl hydrogen polysiloxane fluids and the like, of which dimethyl silicone fluids and methyl hydrogen polysiloxane fluids are preferred.

To summarize the description on the types of the water repellent agents, dimethyl silicone fluids, methyl hydrogen polysiloxane fluids and 3-aminopropyl triethoxy silane are particularly preferable as the surface treatment agent of the filler as the component (B) in the inventive molding composition.

The procedure for the surface treatment of the component (B) with the water repellent agent is not particularly limitative according to any known method conventionally undertaken for the surface treatment of a powdery material. A preferable method in respect of the versatility and controllability of the temperature and mixing velocty in the treatment is to use a Henschel mixer in which the water repellent agent is sprayed on to the filler under agitation and thoroughly mixed together.

The water repellent agent in this surface treatment of the filler as the component (B) should be used in an amount in the range from 0.01 to 5% by weight or, preferably, from 0.05 to 3% by weight or, more preferably, from 0.1 to 2% by weight based on the amount of the filler as the component (B) before the surface treatment. When the amount of the water repellent agent is too small, no sufficient coupling effect can be exhibited between the surface of the filler and the matrix phase so that the resultant molding composition would be poor in the moldability. When the amount thereof is too large, on the other hand, a phenomenon of slipping may be caused due to the excessively strong effect of lubrication between the filler surface and the matrix phase leading to disadvantages of decreased productivity of pelletization of the molding composition and decreased workability in the molding works along with a problem of poor appearance of the shaped articles prepared from the composition as a result of strong bleeding of the water repellent agent on the surface of the shaped article.

The fillers thus surface-treated or coated with the water repellent agent as the component (B) can be used either singly or as a combination of two kinds or more according to need. The compounding amount of the component (B) in the inventive molding composition should be in the range from 30 to 98 parts by wieght or, preferably, from 50 to 97 parts by weight or, more preferably, from 60 to 95 parts by weight per 100 parts by weight of the total amount of the components (A) and (B).

As is mentioned before, the inventive molding composition can be further admixed with a low-molecular oxidized polypropylene as the component (C) in an amount in the range from 0.1 to 2% by weight based on the total amount of the polymeric matrix phase as the component (A) and the filler after the surface treatment as the component (B). The low-molecular oxidized polypropylene is prepared by the oxidative degradation of, for example, an isotactic poly propylene as a solid or melt or in the form of a solution with an oxidizing agent such as peroxides. Carboxyl groups and other types of oxygen-containing groups are

introduced into the molecular structure of the polypropylene by this oxidizing reaction. By virtue of the carboxyl groups introduced into the molecular structure, the low-molecular oxidized polypropylene has increased miscibility with thermoplastic resins having polarity such as polyamides in comparison with non-oxidized low-molecular polypropylenes. It is preferable to use a low-molecular oxidized polypropylene having an average molecular weight in the range from 1500 to 20000. When admixed with an appropriate amount of such a low-molecular oxidized polypropylene, the molding composition is imparted with improved moldability and capable of giving shaped articles having improved mechanical strengths and electric conductivity.

When improvements in the mechanical properties and dimensional stability of shaped articles of the composition are desired, it is sometimes advantageous to admix the composition with a modifier such as a modified polyolefin which serves to increase the affinity between the polymeric matrix as the component (A) and the surface of the filler as the component (B). Suitable polyolefin-based modifiers include, for example, polyethylene and polypropylene modified by graft-polymerization of 0.05 to 20% by weight of a monomer exemplified by unsaturated organic acids and derivatives thereof such as acrylic acid, methacrylic acid, maleic acid, itaconic acid and other organic acids, maleic anhydride, itaconic anhydride, citraconic anhydride and other anhydrides of unsaturated organic acids, methyl acrylate, monomethyl maleate and other esters of unsaturated organic acids, acrylamide, fumaric acid monoamide and other amides of unsaturated organic acids, itaconic acid imide and other imides of unsaturated organic acids, and so on. The modification reaction of the polyolefin by the polymerization of these monomers can be accelerated by an organic peroxide such as benzoyl peroxide, lauroyl peroxide, dicumyl peroxide, tert-butyl hydroperoxide and the like.

Usable modifiers in addition to the above described ones include ethylene-or propylene-based polymers modified by graft polymerization of an unsaturated epoxide such as glycidyl acrylate, glycidyl methacrylate, vinyl glycidyl ether, allyl glycidyl ether and the like carried out optionally with admixture of a liquid rubber such as a polybutadiene hydroxylated at the molecular chain ends.

The amount of these modifiers added to the inventive molding composition should usually be in the range from 1 to 10% by weight based on the total amount of the components (A) and (B). When the amount thereof is too small, the desired improvement by the addition of the modifier cannot be fully exhibited as a matter of course. When the amount thereof is too large, on the other hand, phase separation may sometimes take place in the shaped article of the composition to greatly decrease the mechanical strengths.

It is optional according to need that the molding composition of the invention is further admixed with various kinds of inorganic and organic fillers though in a limited amount not to substantially affect the desirable properties of the composition or the shaped article prepared therefrom. Such an optional filler may be powdery, granular or fibrous.

Inorganic fillers suitable for the above mentioned optional addition are exemplified by oxides such as silica, diatomaceous earth, barium ferrite, beryllium oxide, pumice, pumice balloons and the like, hydroxides such as aluminum hydroxide, magnesium hydroxide, basic magnesium carbonate and the like, carbonates such as calcium carbonate, magnesium carbonate, dolomite, dawsonite and the like, sulfates and sulfites such as calcium sulfate, barium sulfate, ammonium sulfate, calcium sulfite and the like, silicates such as talc, clay, mica, asbestos, glass balloons, glass beads, montmorillonite, bentonite and the like, carbonaceous fillers such as carbon black, graphite powder, carbon balloons and the like, molybdenum sulfide, zinc borate, barium metaborate, calcium borate, sodium borate and the like. These inorganic fillers can be used either singly or as a combination of two kinds or more according to need.

Organic fillers suitable for the above mentioned optional addition are exemplified by non-fibrous ones such as rice hulls, wood flour, fragments of paper and cellophane and the like. These organic fillers also can be used either singly or as a combination of two kinds or more according to need. It is of course optional that inorganic and organic fillers are used in combination.

If desired, the molding composition of the invention can be admixed with various kinds of additives conventionally compounded in resin-based molding compositions including, for example, lubricants, coloring agents, stabilizers, antioxidants, ultraviolet absorbers, antistatic, agents, flame retardant agents, plasticizers, blowing agents and the like according to the intended application of the articles shaped from the molding composition.

The molding composition of the present invention can be prepared by uniformly blending and compounding the components (A) and (B), optionally, together with the component (C) and above described optional additives in a conventional procedure of kneading in a molten condition by using a suitable blending machine such as Henschel mixers, single-or double-screw extruder mahcines, Banbury mixers, roller mixers and the like, of which Henschel mixers, extruder machines and Bunbury mixers are preferred.

The molding composition of the present invention can be shaped into articles by any conventional molding method such as injection molding, extrusion molding, compression molding and the like without particular limitations by virtue of the good moldability. The composition can give not only shaped articles having complicated configuration as molded but also shaped articles suitable for secondary work-ing to meet various applications by adequately modifying the blending ratio of the components. The application fields of the shaped articles of the inventive molding composition include structural and functional parts in electric and electronic instruments, machines in general, automobiles and the like, furnitures, household commodities and so on. Particularly exemplary of the shaped articles are, for example, all kinds of rotatory members for power transmission such as flywheels, gears, pulleys, cams, motors and the like, housings, chassis, turn tables and the like of record players, cassette tape recorders, speaker boxes, etc., sound insulating and shielding materials, vibra-tion dumping materials, shielding materials for electro-magnetic waves, furnitures, kitchenwares, office supplies, toys, fishing implements and so on.

The thermoplastic resin-based molding composition of the present invention is prepared by compounding a thermoplastic polymer as the matrix phase with a metallic filler after a surface treatment with a water repellent agent so that the filler particles dispersed in the polymeric matrix are highly resistant against rusting along with greatly improved affinity between the surface of the filler particles and the matrix polymer. Accordingly, the inventive molding composition has good moldability and is capable of giving shaped articles having outstandingly good outer appearance, excellent mechanical properties, high dimensional stability without warping distortion and stable electric conductivity. By virtue of the improved moldability, the inventive molding composition can be shaped into articles having large dimensions or a complicated configura tion and the shaped articles have good secondary workability suitable for machining with standard machine tools such as cutting, grinding, lathing and the like. Thus, present invention provides a material having excellent moldability into shaped articles and machinability of the shaped articles in combination. Such a combination of moldability and machinability is the very great advantage of the inventive molding composition never obtained in any of conventional resin-based molding compositions and metals.

In the following, examples are given to illustrate the inventive molding compositions in more detail but not to limit the scope of the invention in any way.

In the examples given below, the polymeric materials used as the ploymeric matrix of the molding compositions include the commercially available products listed below, each of which is referred to hereinbelow with the abridged symbol of the name preceding the name of the polymeric material.

(1) 6-PA: 6-nylon, LM-102, a product by Kanegafuchi Chemical Industry Co.
(2) 66-PA: 6,6-nylon, 1200S, a product by Asahi Chemical Industry Co.
(3) 12-PA: 12-nylon, 3014U, a product by Ube Kosan Co.
(4) MXDA: polyamide, 6002, a product by Mitsubishi Gas Chemical Co.
(5) PP: polypropylene, J2000G, a product by Idemitsu Petrochemical Co.
(6) PBT: poly(butylene terephthalate), 5010, a product by Mitsubishi Chemical Industries Co.
(7) PET: poly(ethylene terephthalate), MA 2101, a product by Unitika Co.
(8) POM: polyacetal, 3010, a product by Asahi Chemical Industry Co.
(9) PS: polystyrene, HT-53, a product by Idemitsu Petrochemical Co.
(10) PE: polyethylene, 110J, a product by Idemitsu Petrochemical Co. having a melt index of 14 g/10 minutes
(11) ABS: copolymeric resin of acrylonitrile, butadiene and styrene, JSR-35, a product by Japan Synthetic Rubber Co.
(12) PC: polycarbonate, N-2500, a product by Idemitsu Petrochemical Co.
(13) PVC: poly(vinyl chloride), JZ-102F, a product by Shin-Etsu Polymer Co.
(14) PMMA: poly(methyl methacrylate), 50N, a product by Asahi Chemical Industry Co.
(15) PPO: poly(phenylene oxide), 731J, a product by Engineering Plastics Co.
(16) PSO: polysulfone, P-1700, a product by Nissan Chemical Co.
(17) PI: polyimide, SP-1, a product by DuPont Far East Co.
(18) SBR: styrene-butadiene rubber, JSR-1500, a product by Japan Synthetic Rubber Co.
(19) EPR: ethylene-propylene copolymeric rubber, EP-07P, a product by Japan Synthetic Rubber Co.
(20) SR: silicone rubber, KE-931U, a product by Shin-Etsu Chemical Co.
(21) EVA: ethylene-vinyl acetate copolymeric rubber, Evatate D-3021, a product by Sumitomo Chemical Co.
(22) PEE: polyester-based elastomer, Belprene P-40B, a product by Toyo Spinning Co.
(23) POE: polyolefin-based elastomer, TPE-1500, a product by Sumitomo Chemical Co.

Further, in the following examples, various kinds of fillers were used as listed below.

(1) Zn: zinc powder having an average particle diameter of about 3 µm, a product by Sakai Chemical Co.

(2) ZnO: zinc oxide having an average particle diameter of about 3 µm, a product by Sakai Chemical Co.

(3) Cu: copper powder having an average particle diameter of about 5 µm, a product by Fukuda Kinzoku Hakufun Kogyo Co.

(4) α-Fe: iron powder having an average particle diameter of about 0.5 µm, a product by Dowa Teppun Kogyo Co.

(5) α-Fe_2O_3: iron oxide powder having an average particle diameter of about 0.5 µm, a product by Dowa Teppun Kogyo Co.

(6) Ni: nickel powder having an average particle diameter of about 3 µm

(7) Pb: lead powder having an average particle diameter of 10 µm

(8) Al: aluminum powder having an average particle diameter of about 10 µm

(9) Sn: tin powder having an average particle diameter of about 7 µm

(10) SnO_2: tin oxide powder having an average particle dia meter of about 3 µm

(11) SS: stainless steel powder having an average particle diameter of about 10 µm

(12) SA: powder of solder alloy having an average particle diameter of about 8 µm

(13) BR: brass powder having an average particle diameter of about 10 µm

(14) SF: stainless steel fibers having a diameter of 10 µm and fiber length of 6 mm

(15) NF: nickel fibers having a diameter of 10 µm and fiber length of 8 mm

(16) PT: whiskers of potassium titanate having a diameter of 0.3 µm and length of 15 µm

(17) ZrO_2: zirconia powder having an average particle diameter of about 0.5 µm

The above listed fillers were used each after a surface treatment with one of the water repellent agents shown below.

A: 3-aminopropyl triethoxy silane, a product by Nippon Unicar Co.

B: N-(2-aminoethyl)-3-aminopropyl trimethoxy silane, a product by Nippon Unicar Co.

C: methyl hydrogen polysiloxane fluid, a product by Shin-Etsu Chemical Co.

D: dimethyl silicone fluid, a product by Shin-Etsu Chemical Co.

E: isopropyl triisostearoyl titanate, a product by Ajinomoto Co.

F: isopropyl tri(N-amidoethyl aminoethyl) titanate, a product by Ajinomoto Co.

G: finely divided silica powder having an average particle diameter of about 12 µm, a product by Nippon Aerosil Co.

H: finely divided silica powder having an average particle diameter of about 7 µm, a product by Nippon Aerosil Co.

I: stearic acid

J: stearyl alcohol

K: polyethylene wax

Example 1.

A 0.3 part by weight of 3-aminopropyl triethoxy silane was sprayed to 100 parts by weight of a zinc powder having an average particle diameter of 3 µm contained in a Henschel mixer of 20 liter capacity and the mixer was run for 5 minutes at a velocity of 1000 rpm to mix them together at a temperature of 60 to 100 °C to prepare a surface-coated zinc powder. Thereafter, a 6-PA resin in an amount of 50% by weight based on the surface-coated zinc powder was added to the mixer and melted and mixed together by running the mixer for 15 minutes at a velocity of 2000 rpm and at a temperature of 200 to 300 °C to give a composite molding resin composition with further admixture of 0.3% by weight of an antioxidant (Irganox 1010, a product by Ciba Geigy Co.), 0.3% by weight of calcium stearate as a lubricant (a product by Nippon Yushi Co.) and 1.0% by weight of carbon black (DL-600, a product by Lion Akzo Co.), each amount being based on the total amount of the 6-PA resin and the surface-coated zinc powder.

The thus obtained molding composition was pelletized by using a single-screw extruder machine (Model NVC-50, manufactured by Nakatani Machinery Co.) operated at a temperature of 200 to 300 °C with a rate of extrusion of 30 kg/hour and the pellets were shaped into test plates by injection molding using an injection molding machine (Model FS-160S, manufactured by Nissei Resin Industry Co.) at a temperature of 200 to 300 °C.

The test plates were subjected to the evaluation of various properties including the following items each according to the procedure described below. The results are shown in Table 1.

(1) Resistance against rusting

A test plate of 75 mm by 75 mm wide and 3.2 mm thick was put into a bag made of a polyethylene film of 40 μm thickness and, after sealing of the opening by welding, the bag was heated for 100 hours or 300 hours in an atmosphere of 95% relative humidity at 60 °C. The test plate taken out of the bag was inspected for the surface condition with naked eyes or by using a magnifying lens of 25 magnification to give the results in four ratings of A, B, C and D according to the following criteria.

A: no rust found under magnifying lens
B: powder-like rust found under magnifying lens
C: small number of rust speckles found with naked eyes
D: large number of rust speckles found with naked eyes

(2) Moldability

A box having outer dimensions of 150 mm by 80 mm by 80 mm with a wall thickness of 5 mm was shaped from the molding composition by injection molding using the same injection molding machine as used in the preparation of the test plates above to determine the critical impregnation pressure or minimum impregnation pressure for short shot in kg/cm². The thus molded boxes were visually inspected for the outer appearance and the results were expressed in three ratings of A, B and C according to the following criteria.

A: beautiful and acceptable
B: small number of silver marks found
C: large number of silver marks found

(3) Izod impact strength

Measurement was performed according to ASTM D-1302 to give the results in kg cm/cm.

(4) Electric resistance

Measurement was performed according to JIS C 1302 by using an automatic insulation-resistance tester (Model F-535F, manufactured by Fuso Electric Co.) with a voltage impression of 500 volts DC to give the total resistance in megaohm.

Examples 2 to 65 and Comparative Examples 1 to 6.

The experimental procedure in each of these Examples and Comparative Examples was substantially the same as in Example 1 using the same zinc powder as the filler excepting replacement of the 6-PA resin as the matrix polymer and the 3-aminopropyl triethoxy silane as the water repellent agent each with the material shown in Table 1 in an amount also indicated in the same table. In the formulations shown in Table 1, the amounts of the filler and the matrix polymer given in parts by weight are given per 100 parts by weight of the total amount of the filler after the surface treatment and the matrix polymer and the amount of the water repellent agent given in % by weight is based on the amount of the filler before the surface treatment. The molding compositions prepared in Comparative Examples 2 and 4 were disadvantageous in respect of the low productivity in pelletization due to slipping. Table 1 also shows the results of the evaluation of the products carried out in the same manner as in Example 1. In Examples 64 and 65, the zinc powder as the filler and the finely divided silica powder as the water repellent agent were dry-blended in the Henschel mixer operated at a velocity of 1000 rpm for 5 minutes at a temperature of 60 to 100 °C before the addition of the 6-PA resin.

Table 1 (Part 1)

		Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability		Izod impact test		Electric resistance, megaohm
					100 hours	300 hours	Minimum pressure, kg/cm²	Appearance	Notched, kg·cm/cm	Unnotched, kg·cm/cm	
Example	1	Zn (50)	A (0.3)	6-PA (50)	A	A	31	A	10.2	62	16
	2	Zn (70)	A (0.3)	6-PA (30)	A	A	34	A	8.9	53	14
	3	Zn (90)	A (0.3)	6-PA (10)	A	A	40	A	7.5	46	0.5
	4	Zn (95)	A (0.3)	6-PA (5)	A	A	45	B	5.7	33	0.3
	5	Zn (90)	A (1.0)	6-PA (10)	A	A	39	A	7.6	46	0.4
	6	Zn (90)	A (3.0)	6-PA (10)	A	A	35	A	7.9	48	0.3
	7	Zn (90)	A (0.3)	66-PA (10)	A	A	42	A	7.4	48	0.7
	8	Zn (70)	A (0.3)	PP (30)	A	A	34	A	10.0	78	13
	9	Zn (80)	A (0.3)	PP (20)	A	A	37	A	8.1	70	10
	10	Zn (95)	A (0.3)	PP (5)	A	A	42	A	7.4	61	0.5
	11	Zn (90)	A (0.3)	PBT (10)	A	A	45	A	6.7	41	0.6
	12	Zn (90)	A (0.3)	PET (10)	A	A	46	A	6.1	42	1.1
	13	Zn (90)	A (0.3)	POM (10)	A	A	43	A	7.7	47	0.9
	14	Zn (90)	A (0.3)	PE (10)	A	A	39	A	9.2	77	2.7
	15	Zn (90)	A (0.3)	ABS (10)	A	A	41	A	11.4	73	1.6

Table 1 (Part 2)

		Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability		Izod impact test		Electric resistance, megaohm
					100 hours	300 hours	Minimum pressure kg/cm^2	Appearance	Notched, kg·cm/cm	Unnotched, kg·cm/cm	
Example	18	Zn (90)	B (0.3)	6-PA (10)	A	A	41	A	6.9	41	0.5
	19	Zn (90)	C (0.05)	6-PA (10)	A	B	49	A	6.7	43	12
	20	Zn (90)	C (0.5)	6-PA (10)	A	A	41	A	7.1	44	0.3
	21	Zn (90)	C (2.0)	6-PA (10)	A	A	39	A	7.7	47	0.4
	22	Zn (90)	C (0.5)	PP (10)	A	A	37	A	8.7	52	0.9
	23	Zn (90)	C (0.5)	PBT (10)	A	A	39	A	6.9	40	0.7
	24	Zn (90)	C (0.5)	POM (10)	A	A	37	A	6.9	49	0.7
	25	Zn (90)	C (0.5)	ABS (10)	A	A	37	A	11.7	71	0.6
	44	Zn (90)	D (0.5)	6-PA (10)	A	A	43	A	6.4	40	1.2
	62	Zn (90)	E (0.5)	6-PA (10)	A	A	44	A	6.1	37	1.7
	63	Zn (90)	F (0.5)	6-PA (10)	A	A	44	A	6.0	37	2.0
	17	Zn (90)	A (0.5)	6-PA/PP 5/5(10)	A	A	43	A	7.9	48	1.2
	27	Zn (90)	C (0.5)	6-PA/PET= 5/5(10)	A	A	45	A	6.3	41	1.5
	28	Zn (90)	C (0.5)	12-PA(10)	A	A	35	A	6.6	41	0.3
	29	Zn (90)	C (0.5)	PS (10)	A	A	42	A	6.1	40	0.3

Table 1 (Part 3)

		Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability		Izod impact test		Electric resistance, megaohm
					100 hours	300 hours	Minimum pressure, kg/cm^2	Appearance	Notched, kg·cm/cm	Unnotched, kg·cm/cm	
Example	30	Zn (90)	C (0.5)	PC (10)	A	A	44	A	11.9	77	1.5
	31	Zn (90)	C (0.5)	PVC (10)	A	A	37	A	9.7	70	0.2
	32	Zn (90)	C (0.5)	PMMA (10)	A	A	33	A	5.9	37	2.4
	33	Zn (90)	C (0.5)	PPO (10)	A	A	44	A	6.3	44	1.1
	34	Zn (90)	C (0.5)	PSO (10)	A	A	51	A	7.1	45	1.0
	35	Zn (90)	C (0.5)	PI (10)	A	A	51	A	7.4	60	1.7
	36	Zn (90)	C (0.5)	PPS (10)	A	A	53	A	6.2	43	1.9
	37	Zn (90)	C (0.5)	SBR (10)	A	A	37	A	17.1	105	0.1
	38	Zn (90)	C (0.5)	EPR (10)	A	A	32	A	14.9	90	0.1
	39	Zn (90)	C (0.5)	SR (10)	A	A	40	A	13.7	88	3.3
	40	Zn (90)	C (0.5)	EVA (10)	A	A	35	A	15.2	94	0.4
	41	Zn (90)	C (0.5)	PEE (10)	A	A	39	A	11.7	75	0.5
	42	Zn (90)	C (0.5)	POE (10)	A	A	36	A	14.2	89	0.5
	64	Zn (90)	G (0.5)	6-PA (10)	A	A	39	A	6.3	42	0.9
	65	Zn (90)	H (0.5)	6-PA (10)	A	A	38	A	6.5	44	0.8

Table 1 (Part 4)

		Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability		Izod impact test		Electric resistance, megaohm
					100 hours	300 hours	Minimum pressure, kg/cm²	Appearance	Notched, kg·cm/cm	Unnotched, kg·cm/cm	
Example	45	Zn (50)	D (0.5)	66-PA (50)	A	A	34	A	11.5	64	15
	46	Zn (70)	D (0.5)	66-PA (30)	A	A	35	A	9.2	56	14
	47	Zn (90)	D (0.5)	66-PA (10)	A	A	41	A	7.5	49	0.7
	48	Zn (95)	D (0.5)	66-PA (5)	A	A	47	A	5.9	35	0.3
	49	Zn (90)	D (1.0)	66-PA (10)	A	A	39	A	7.9	50	0.7
	50	Zn (90)	D (3.0)	66-PA (10)	A	A	37	A	8.0	51	0.6
	51	Zn (50)	D (0.5)	12-PA (50)	A	A	30	A	9.7	55	14
	52	Zn (90)	D (0.5)	12-PA (30)	A	A	32	A	8.0	49	12
	53	Zn (90)	D (0.5)	12-PA (10)	A	A	33	A	6.9	44	0.3
	54	Zn (95)	D (0.5)	12-PA (5)	A	A	39	A	5.0	30	0.3
	55	Zn (90)	D (1.0)	12-PA (10)	A	A	31	A	7.0	45	0.3
	56	Zn (90)	D (3.0)	12-PA (10)	A	A	30	A	7.1	45	0.3
	16	Zn (90)	D (3.0)	12-PA (10)	A	A	34	A	6.7	42	0.4
	26	Zn (90)	C (0.5)	66-PA (10)	A	A	41	A	7.5	50	0.7
	57	Zn (90)	D (0.5)	66-PA (10)	A	A	35	A	8.9	54	0.6

T a b l e 1 (Part 5)

		Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability		Izod impact test		Electric resistance, megaohm
					100 hours	300 hours	Minimum pressure, kg/cm²	Appearance	Notched, kg·cm/cm	Unnotched, kg·cm/cm	
Example	58	Zn (90)	D (0.5)	66-PA (10)	A	A	37	A	7.0	41	0.6
	43	Zn (90)	C (0.5)	6PA/PP= 5/5(10)	A	A	42	A	8.1	50	1.1
	59	Zn (90)	D (0.5)	6-PA/PP= 5/5(10)	A	A	40	A	8.2	53	1.0
	60	Zn (70)	D (0.5)	6-PA/PP= 5/5(30)	A	A	33	A	8.9	54	15
	61	Zn (50)	D (0.5)	6-PA/PP= 5/5(50)	A	A	30	A	10.5	64	16
Comparative Example	1	Zn (90)	A (0.005)	6-PA (10)	C	D	51	C	4.3	19	1.0
	2	Zn (90)	A (6.0)	6-PA (10)	A	A	35	C	6.1	41	29
	3	Zn (90)	C (0.005)	6-PA (10)	C	D	67	B	4.7	22	35
	4	Zn (90)	C (6.0)	6-PA (10)	A	A	35	C	6.0	39	27
	5	Zn (25)	A (0.3)	6-PA (75)	A	A	28	A	13.1	73	100<
	6	Zn (99)	A (0.3)	6-PA (1)	B	C	61	C	1.9	10	40

Examples 66 to 103 and Comparative Examples 7 to 13.

The experimental procedure in each of these Examples and Comparative Examples was substantially the same as in Example 1. Table 2 below shows the formulation of the molding compositions and the results of evaluation undertaken in the same manner as in Example 1.

Examples 104 to 107 and Comparative Examples 14 and 15.

A molding resin composition was prepared by first blending, in a Henschel mixer of 20 liter capacity, 15 parts by weight of a 6-PA resin, 85 parts by weight of a ZnO powder having a varied average particle diameter shown in Table 3 below, 0.5 part by weight of a low-molecular oxidized polypropylene having an average molecular weight of 3500 and 0.3 part by weight of an aminosilane-based coupling agent and then kneading the blend thoroughly at 220 to 350 °C in a double-screw kneading machine (Model NAS-50, manufactured by Nakatani Machinery Co.).

The thus prepared molding resin compositions were each shaped by injection molding into test plates at 220 to 350 °C using the same injection molding machine as used in Example 1. The molding compositions were evaluated by measuring the minimum molding pressure in the injection molding of the composition and the mechanical and electrical properties of the test plates in the following manner. The results are shown in Table 3.

Table 2 (Part 1)

		Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability		Izod impact test		Electric resistance, megaohm
					100 hours	300 hours	Minimum pressure, kg/cm²	Appearance	Notched, kg·cm/cm	Unnotched, kg·cm/cm	
Example	66	ZnO (90)	C (0.5)	6-PA (10)	A	A	43	A	7.1	42	-
	71	ZnO (90)	A (0.5)	6-PA (10)	A	A	41	A	7.0	42	-
	84	Cu (90)	C (0.5)	6-PA (10)	A	A	47	A	8.7	48	17
	85	Cu (90)	A (0.5)	6-PA (10)	A	A	45	A	8.9	50	19
	86	Fe (90)	C (0.5)	6-PA (10)	A	A	48	A	6.1	39	15
	87	Fe (90)	A (0.5)	6-PA (10)	A	A	44	A	6.3	40	15
	88	Fe_2O_3 (90)	C (0.5)	6-PA (10)	A	A	49	A	5.7	38	5.4
	89	Fe_2O_3 (90)	A (0.5)	6-PA (10)	A	A	44	A	5.9	41	7.0
	90	Zn/Fe_2O_3 =45/45 (90)	A (0.5)	6-PA (10)	A	A	44	A	6.0	35	0.7
	91	Zn/ZnO =70/20 (90)	C (0.5)	6-PA (10)	A	A	40	A	7.2	44	1.0
	92	Ni (90)	C (0.5)	6-PA (10)	A	A	43	A	6.4	35	0.2
	93	Pb (90)	C (0.5)	6-PA (10)	A	A	42	A	7.9	48	1.4
	94	Aℓ (90)	C (0.5)	6-PA (10)	A	A	39	A	8.2	50	1.9
	95	Sn (90)	C (0.5)	6-PA (10)	A	A	44	A	7.1	44	0.3

Table 2 (Part 2)

		Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability		Izod impact test		Electric resistance, megaohm
					100 hours	300 hours	Minimum pressure, kg/cm^2	Appearance	Notched, kg·cm/cm	Unnotched, kg·cm/cm	
Example	96	SnO_2 (90)	C (0.5)	6-PA (10)	A	A	46	A	6.0	38	0.3
	97	SnO_2 (90)	C (0.5)	6-PA (10)	A	A	39	A	6.4	44	0.2
	98	SnO_2 (90)	C (0.5)	6-PA (10)	A	A	37	A	7.2	46	0.5
	99	SnO_2 (90)	C (0.5)	6-PA (10)	A	A	38	A	6.6	45	0.3
	100	SnO_2 (90)	C (0.5)	6-PA (10)	A	A	52	A	5.4	35	0.1
	101	SnO_2 (90)	C (0.5)	6-PA (10)	A	A	51	A	5.9	37	0.1
	102	SnO_2 (90)	C (0.5)	6-PA (10)	A	A	42	A	6.7	41	0.9
	103	SnO_2 (90)	C (0.5)	6-PA (10)	A	A	47	A	6.9	45	2.1
Comparative Example	7	Fe_2O_3 (90)	C (0.005)	6-PA (10)	C	D	69	C	1.7	12	50
	8	Fe_2O_3 (90)	A (0.005)	6-PA (10)	C	D	71	C	2.3	14	70
	9	Zn (90)	A (0.5)	6-PA (10)	B	C	59	B	4.3	21	75
	10	Zn (90)	C (0.5)	6-PA (10)	A	B	62	B	3.1	16	10
	11	Zn (90)	G (0.5)	6-PA (10)	C	D	57	B	3.2	17	100<
	12	Fe_2O_3 (90)	A (0.5)	6-PA (10)	B	C	61	B	2.0	15	100<
	13	Fe (90)	C (0.5)	6-PA (10)	B	B	64	B	2.3	16	11

(1) Molding pressure: a box having dimensions of 90 mm by 150 mm by 70 mm with a wall thickness of 5 mm and a pin gate of 1 mm diameter was shaped by injection molding under the above mentioned conditions to determine the minimum pressure for impregnation in kg/cm^2G.

(2) Mechanical properties: tensile strength in kg/cm^2 of the test plates was determined according to ASTM D-638 and flexural strength and elastic modulus by bending each in kg/cm^2 were determined according to ASTM D-790.

(3) Electrical properties: specific resistance in ohm-cm was determined according to Japan Rubber Association Standard SRJS-2301-1969.

Table 3

		Average Particle diameter of ZnO, µm	Molding pressure, kg/cm^2G	Tensile strength, kg/cm^2	Flexural strength, kg/cm^2	Elastic modulus by bending, $\times 10^4$ kg/cm^2	Specific resistance, ohm·cm
Example	104	0.3	75	860	1510	12.8	1×10^5
	105	1	70	810	1450	12.5	1×10^5
	106	3	67	795	1320	11.7	1×10^5
	107	5	65	710	1250	10.9	1×10^5
Comparative Example	14	0.1	97	905	1570	13.1	1×10^5 *
	15	9	60	650	990	9.1	1×10^5

* large variation in the values of specific resistance

In these Examples and Comparative Examples, the low-molecular oxidized polypropylene was a commercial product (Biscol TS-200, a product by Sanyo Kasei Co.) and the aminosilane-based coupling agent was aminopropyl triethoxy silane.

Examples 108 to 110 and Comparative Examples 16 and 17.

The formulation and experimental procedure in each of these Examples and Comparative Examples were substantially the same as in Examples 104 to 107 except that the amounts of the 6-PA resin and ZnO, having an average particle diameter of 2 μm, were varied as shown in Table 4 below, which also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples.

Table 4

		6-PA, parts by weight	ZnO, parts by weight	Molding pressure, kg/cm^2G	Tensile strength, kg/cm^2	Flexural strength, kg/cm^2	Elastic modulus by bending, $\times 10^4$ kg/cm^2	Specific resistance, ohm·cm
Example	108	40	60	61	870	1550	9.2	1×10^7
	109	20	80	68	875	1470	12.1	1×10^5
	110	5	95	74	760	1350	13.5	1×10^4
Comparative Example	16	60	40	49	920	1660	7.4	1×10^{11}
	17	3	97	150	620	1290	14.6	1×10^4

Examples 111 to 113 and Comparative Examples 18 and 19.

The formulation and experimental procedure were substantially the same as in the preceding examples except that the amounts of the 6-PA resin and ZnO filler were 15 parts by weight and 85 parts by weight, respectively, in each of these Examples and Comparative Examples and the amount of the low-molecular oxidized polypropylene, referred to as the component (C) hereinbelow, was varied as indicated in Table 5 below, which also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples.

Table 5

		Component (C), parts by weight	Molding pressure, kg/cm²G	Tensile strength, kg/cm²	Flexural strength, kg/cm²	Elastic modulus by bending, x 10^4 kg/cm²	Specific resistance, ohm·cm
Example	111	0.1	90	705	1120	10.1	1 x 10^5
	112	0.7	67	830	1490	12.7	1 x 10^5
	113	1.5	59	755	1300	11.6	1 x 10^5
Comparative Example	18	0.05	120	520	950	9.7	1 x 10^7
	19	2.5	51	670	970	9.6	1 x 10^5

Examples 114 to 117.

The formulation and experimental procedure in each of these Examples were substantially the same as in the preceding examples except that the amount of the component (C) was always 0.5 part by weight and, instead, the average molecular weight thereof was varied as indicated in Table 6 given below, which also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples.

Table 6

		Average molecular weight of component (C)	Molding pressure, g/cm^2G	Tensile strength, kg/cm^2	Flexural strength, kg/cm^2	Elastic modulus by bending, $\times 10^4$ kg/cm^2	Specific resistance, ohm·cm
Example	114	7000	75	815	1460	12.7	1×10^5
	115	15000	72	820	1470	12.9	1×10^5
	116	20000	80	830	1500	13.1	1×10^5
	117	25000	90	845	1510	13.4	1×10^5

Examples 118 to 120 and Comparative Examples 20 and 21.

The formulation and experimental procedure in each of these Examples and Comparative Examples were substantially the same as in the preceding examples except that the low-molecular oxidized polypropylene as the component (C) always had an average molecular weight of 3500 and the amount of the 3-aminopropyl triethoxy silane as the aminosilane-based coupling agent was varied as indicated in Table 7 below, which also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples.

Table 7

		Aminosilane, parts by weight	Molding pressure, kg/cm^2 G	Tensile strength, kg/cm^2	Flexural strength, kg/cm^2	Elastic modulus by bending, $\times 10^4$ kg/cm^2	Specific resistance, ohm·cm
Example	118	0.1	87	760	1310	11.9	1×10^5
	119	0.7	65	830	1490	13.0	1×10^5
	120	1.5	61	760	1310	12.1	1×10^5
Comparative Example	20	0.05	105	550	970	10.1	1×10^7
	21	2.5	57	720	960	10.5	1×10^8 *

* large variation in the values as measured

Examples 121 to 134.

The formulation and experimental procedure in each of these Examples were substantially the same as in the preceding Examples except that the amount of the 3-aminopropyl triethoxy silane was always 0.3 part by weight and the thermoplatic resin, taken in an amount of 15 parts by weight, was not the 6-PA resin but one of the polymers or a combination of two polymers in a proportion as indicated in Table 8 below, which also shows the results of evaluation of the molding compositions carried out in the same manner as in the preceding examples. The values of specific resistance of the test plates were each 1 x 10^5 ohm•cm.

Table 8

		Polymer(s) (ratio by weight)	Molding pressure, kg/cm^2 G	Tensile strength, kg/cm^2	Flexural strength, kg/cm^2	Elastic modulus by bending, x 10^4 kg/cm^2
Example	121	66-PA	73	820	1470	12.9
	122	MXDA	75	840	1500	13.0
	123	PET	73	890	1620	13.4
	124	PBT	74	795	1240	11.1
	125	PPO	77	810	1450	12.7
	126	PC	76	835	1490	12.9
	127	ABS	67	720	1150	10.1
	128	POM	70	805	1390	12.0
	129	PP	47	510	910	6.2
	130	PE	44	460	810	5.4
	131	PPO/6-PA (9:6)	74	830	1490	12.9
	132	PC/PET (10:5)	74	870	1520	12.9
	133	PBT/PET (9:6)	74	850	1430	12.7
	134	PSO	85	810	1350	13.1

Examples 135 to 139.

The formulation and experimental procedure in each of these Examples were substantially the same as in the preceding Examples except that the polymer for the matrix was one of those indicated in Table 9 below and 0.3 part by weight of 3-aminopropyl triethoxy silane was replaced with 0.5 part by weight of a dimethyl silicone fluid. Table 9 below also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples. The values of specific resistance of the test plates were each 1 x 10^5 ohm•cm.

Table 9

Example	Polymer	Molding pressure, kg/cm^2G	Tensile strength, kg/cm^2	Flexural strength, kg/cm^2	Elastic modulus by bending, x 10^4 kg/cm^2
135	6-PA	65	795	1390	12.3
136	12-PA	61	720	1190	11.7
137	66-PA	71	835	1510	13.1
138	PBT	71	815	1290	11.9
139	PP	44	525	990	6.4

Examples 140 to 144.

The formulation and experimental procedure in each of these Examples were substantially the same as in the preceding Examples except that the polymer for the matrix phase was one of those indicated in Table 10 below and the dimethyl silicone fluid was replaced with the same maount of isopropyl triisostearoyl titanate as a titanate-based coupling agent. Table 10 below also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples. The values of specific resistance of the test plates were each 1 x 10^5 ohm•cm.

Table 10

Example	Polymer	Molding pressure, kg/cm²G	Tensile strength, kg/cm²	Flexural strength, kg/cm²	Elastic modulus by bending, x 10^4 kg/cm²
140	6-PA	71	805	1410	12.9
141	12-PA	66	700	1190	10.1
142	66-PA	72	840	1530	13.3
143	PBT	73	815	1280	12.0
144	PP	46	510	975	6.1

Preparation Example 1 (Preparation of modified polypropylene)

Into a three-necked flask equipped with a stirrer, thermometer and reflux condenser and having a separable cover were introduced 100 parts by weight of a polypropylene resin having a density of 0.91 g/cm^3 and a melt index MI of 8 g/10 minutes (J700G, a product by Idemitsu Petrochemical Co.), 5 parts by weight of a 1,4-polybutadiene having a number-average molecular weight of 3000 and terminated at each molecular chain end with a hydroxy group (Poly bd R45HT, a product by ARCO Chem. Div.), 20 parts by weight of maleic anhydride, 1.72 parts by weight of dicumyl peroxide and 600 parts by weight of xylene and the mixture was heated under agitation at 120 °C for 1 hour and then at 140 C° for 3 hours to effect the reaction.

After completion of the reaction, the reaction mixture was poured into a large volume of acetone and the precipitates formed in acetone were collected by filtration with suction and dried at 70 °C for 50 hours to give a white powder. This powder was subjected to extraction with acetone in a Soxhlet extractor for 16 hours to give a modified polypropylene as the product by removing unreacted polybutadiene and maleic anhydride.

Examples 145 to 172 and Comparative Examples 22 to 29.

A Henschel mixer was charged with 10 parts by weight of one of the fibrous fillers indicated in Table 11, 70 parts by weight of a zinc powder having an average particle diameter of about 3 μm and 0.5 part by weight of a dimethyl silicone fluid and operated at a velocity of 1000 rpm for 5 minutes at a temperature of 60 to 100 °C to coat the surface of the fibers and zinc particles with the silicone fluid. Thereafter, 20 parts by weight of a 6-PA resin were introduced into the mixer and thoroughly blended together. The thus obtained blend was further kneaded at 220 to 350 °C in a double-screw extruder machine to give a molding resin composition which was then shaped into test plates at 220 to 350 °C by injection molding using the same injection machine as used in Example 1. The molding resin compositions were evaluated for the moldability of the composition, mechanical properties of the test plates, molding shrinkage of the molded articles and warping distortion of the molded articles in the following manner.

(1) Moldability of the molding composition

A box having dimensions of 90 mm by 150 mm by 70 mm with a wall thickness of 5 mm and a pin gate of 1 mm diameter was shaped from the molding composition by injection molding using an injection molding machine (Model IS-125, manufactured by Toshiba Machines Co.) operated under the standard conditions of a cylinder temperature of 220 to 300 °C, temperature of metal mold of 75 to 100 °C, injection pressure of 60 kg/cm^2 and shot time of 20 seconds and the moldability of the molding composition was evaluated according to the following criteria in three ratings in terms of the reproducibility of the box configuration by the injection molding and the injection pressure.

A: quite satisfactory

B: appearance of sink marks at some portions, somewhat higher injection pressure than the standard pressure

C: partly incomplete box configuration, injection pressure of 100 kg/cm^{2}G or higher

(2) Mechanical properties of the test plates

Tensile strength was determined according to ASTM D-638, Izod impact value was determined according to ASTM D-256 and flexural strength and elastic modulus by bending were determined according to ASTM D-790.

(3) Molding shrinkage of molded articles

Square test plates of 76 mm by 76 mm wide and 3.2 mm thick were shaped from the molding composition by injection molding under a sufficiently high injection pressure and the changes of the dimensions in % were determined in the molding direction (MD) and transverse direction (TD).

(4) Warping distortion of shaped articles

A circular disc of 45 mm diameter and 2 mm thickness was shaped by injection molding under the same conditions as above and warping of the disc was evaluated by the height α of the highest point when the disc was placed on a horizontal plane. The results were given in three ratings of A, B and C according to the following criteria.

A: $\alpha < 0.5$ mm
B: 0.5 mm $\leq \alpha \leq$ 1 mm
C: $\alpha > 1$ mm

Table 11 given below shows the formulation of the molding resin compositions and the results of the evaluation thereof performed in the above described manner. In Table 11, the kinds of the fibrous fillers are indicated with the symbols of GF, SF, BF, PT, CF, SCF and APAF for glass fibers, stainless steel fibers, brass fibers, whiskers of potassium titanate, carbon fibers, silicon carbide fibers and aromatic polyamide fibers, respectively.

Table 11 (Part 1)

		Fibrous filler				Tensile strength, kg/cm^2	Izod impact value, kg·cm/cm	Flexural strength, kg/cm^2
		Kind	Length, mm	Diameter, μm	Aspect ratio			
Example	145	GF	10	4	2500	1650	101	2450
	146		10	13	770	1550	94	2300
	147		6	4	1500	1600	97	2350
	148		6	13	462	1570	94	2250
	149		3	4	750	1530	94	2280
	150		3	12	231	1500	94	2200
	151		1	4	250	1500	90	2150
	152		1	13	77	1350	80	2050
	153	SF	10	30	333	1450	77	1900
	154		10	60	167	1300	73	1810
	155		6	30	200	1330	73	1800
	156		6	60	100	1200	66	1760
	157		3	30	100	1200	65	1720
	158		3	60	50	1150	60	1670
	159	BF	10	30	333	1430	75	1900
	160		10	60	167	1290	71	1820
	161		6	30	200	1300	71	1790
	162		6	60	100	1210	66	1720
	163		3	30	100	1190	64	1710
	164		3	60	50	1110	61	1650

Table 11 (Part 2)

		Elastic modulus by bending, x 10^4 kg/cm^2	Molding shrinkage, %		Warping distortion	Moldability	Density, g/cm^3
			M D	T D			
Example	145	12.7	0.82	0.45	B	B	3.21
	146	12.2	0.80	0.45	A	A	3.21
	147	12.0	0.79	0.45	A	A	3.21
	148	12.1	0.80	0.45	A	A	3.21
	149	12.1	0.80	0.45	A	A	3.21
	150	11.5	0.82	0.52	A	A	3.21
	151	10.9	0.82	0.51	A	A	3.21
	152	10.1	0.85	0.60	A	A	3.21
	153	12.5	0.91	0.55	A	A	3.49
	154	12.0	0.89	0.54	A	A	3.49
	155	11.9	0.86	0.54	A	A	3.49
	156	11.6	0.85	0.58	A	A	3.49
	157	11.6	0.85	0.57	A	A	3.49
	158	11.3	0.85	0.61	A	A	3.49
	159	12.7	0.92	0.57	A	A	3.50
	160	11.9	0.90	0.55	A	A	3.50
	161	11.9	0.87	0.54	A	A	3.50
	162	11.4	0.86	0.56	A	A	3.50
	163	11.4	0.85	0.58	A	A	3.50
	164	11.1	0.85	0.63	A	A	3.50

T a b l e 11 (Part 3)

		Fibrous filler				Tensile strength, kg/cm²	Izod impact value, kg·cm/cm	Flexural strength, kg/cm²
		Kind	Length, mm	Diameter, μm	Aspect ratio			
Example	165	PT	0.01	0.1	100	1250	100	1750
	166		0.02	0.1	200	1310	105	1810
	167	CF	10	10	1000	1820	109	1950
	168		3	10	300	1650	102	1800
	169	SCF	10	10	1000	2030	111	2590
	170		3	10	300	1910	104	2400
	171	APAF	6	12	500	1850	109	2100
	172		3	12	250	1710	104	1980
Comparative Example	22	GF	12	4	3000	1710	105	2550
	23		0.12	4	30	820	51	1270
	24	SF	30	10	3000	1500	79	2050
	25		0.3	10	30	710	47	980
	26	BF	30	10	3000	1410	71	1990
	27		0.3	10	30	660	40	900
	28	CF	30	10	3000	1900	110	2050
	29		0.3	10	30	790	59	1110

Table 11 (Part 4)

		Elastic modulus by bending, x 10^4 kg/cm²	Molding shrinkage, %		Warping distortion	Moldability	Density, g/cm³
			M D	T D			
Example	165	10.0	0.75	0.44	A	A	3.30
	166	10.5	0.75	0.45	A	A	3.30
	167	9.7	0.80	0.45	A	A	2.97
	168	8.1	0.80	0.45	A	A	2.97
	169	15.4	0.78	0.42	A	A	3.28
	170	14.2	0.80	0.44	A	A	3.28
	171	10.9	0.80	0.45	A	A	2.92
	172	9.2	0.80	0.45	A	A	2.92
Compar-ative Example	22	12.9	0.90	0.45	C	B	3.21
	23	7.7	0.79	0.57	A	A	3.21
	24	12.7	0.93	0.55	C	B	3.49
	25	7.1	0.81	0.59	A	A	3.49
	26	12.4	0.93	0.55	C	B	3.50
	27	6.9	0.82	0.59	A	A	3.50
	28	10.6	0.89	0.43	C	B	2.97
	29	8.2	0.75	0.42	A	A	2.97

Examples 173 to 183 and Comparative Examples 30 to 39.

The experimental procedure in each of these Examples and Comparative Examples was substantially the same as in the preceding examples except that each of the molding resin compositions was compounded from 20 parts by weight of the 6-PA resin, a varied amount as indicated in Table 12 below of a zinc powder having an average particle diameter of about 3 μm and a varied amount of a fibrous filler, i.e. glass fibers (GF), stainless_steel fibers (SF), potassium titanate whiskers (PT) or carbon fibers (CF), as indicated in Table 12. The results of the evaluation of these molding resin compositions are also shown in Table 12 for the same items as in Table 11 in the preceding examples.

Table 12 (Part 1)

		Zinc powder, parts by weight	Fibrous filler			Tensile strength, kg/cm²	Izod impact value, kg·cm/cm	Flexural strength, kg/cm²
			Kind	Aspect ratio	Parts by weight			
Example	173	75	GF	750	5	1270	80	1770
	174	50		750	30	1890	110	2670
	175	75		231	5	1210	80	1690
	176	50		231	30	1820	97	2570
	177	75	SF	200	5	1110	69	1520
	178	50		200	30	1690	87	2050
	179	75	PT	200	5	1190	90	1620
	180	50		200	30	1590	118	2300
	181	75	CF	300	5	1400	91	1690
	182	50		300	30	1870	105	2010
	183	30		300	40	1990	111	2220
Comparative Example	30	79	GF	750	1	870	59	1260
	31	20		750	60	2110	115	2790
	32	79		231	1	800	57	1200
	33	20	SF	231	60	2050	111	2550
	34	79		200	1	810	47	1020
	35	20		200	60	1820	89	2560
	36	79	PT	200	1	770	79	1090
	37	20		200	60	1780	121	2520
	38	79	CF	300	1	900	79	1110
	39	20		300	60	2110	114	2300

Table 12 (Part 2)

		Elastic modulus by bending, x 10⁴ kg/cm²	Molding shrinkage, % M D	Molding shrinkage, % T D	Warping distortion	Moldability	Density, g/cm³
Example	173	10.9	0.85	0.50	A	A	3.34
	174	13.2	0.75	0.44	A	A	2.80
	175	10.1	0.85	0.51	A	A	3.34
	176	12.7	0.74	0.43	A	A	2.80
	177	10.0	0.88	0.55	A	A	3.45
	178	12.1	0.79	0.50	A	A	3.52
	179	8.9	0.79	0.47	A	A	3.39
	180	12.2	0.71	0.41	A	A	3.02
	181	7.2	0.83	0.46	A	A	3.20
	182	10.9	0.77	0.44	A	A	2.30
	183	11.7	0.76	0.44	A	A	1.75
Comparative Example	30	8.2	1.00	0.81	C	A	3.45
	31	15.4	0.70	0.41	A	C	2.48
	32	7.9	1.01	0.83	C	A	3.45
	33	14.0	0.73	0.42	A	C	2.48
	34	7.9	1.00	0.82	C	A	3.47
	35	13.7	0.75	0.47	A	C	3.56
	36	7.1	1.00	0.79	C	A	3.45
	37	13.9	0.70	0.40	A	C	2.77
	38	6.2	1.01	0.80	C	A	3.41
	39	12.8	0.75	0.43	A	C	1.89

Examples 184 to 204 and Comparative Examples 40 to 45.

The experimental procedure in each of these Examples and Comparative Examples was substantially the same as in the preceding examples except that the molding resin compositions were each compounded from 20 parts by weight of the 6-PA resin, 10 parts by weight of glass fibers having an aspect ratio of 231 and 70 parts by weight of a particulate filler indicated in Table 13 below, which also shows the results of the evaluation of the molding compositions.

Examples 205 to 223.

The experimental procedure in each of these Examples was substantially the same as in Examples 145 to 172 except that the molding resin compositions were each compounded from 10 parts by weight of glass fibers having an aspect ratio of 231, 70 parts by weight of zinc powder having an average particle diameter of about 3 µm and 20 parts by weight of one kind or a combination of two kinds of the thermoplastic resins indicated in Table 14 below, which also shows the results of the evaluation of the molding compositions. When two kinds of the thermoplastic resins were used, they were taken in equal amounts.

Table 13

		Particulate filler: Kind	Particulate filler: Average particle diameter, µm	Izod impact strength, kg•cm/cm	Warping distortion	Moldability	Density, g/cm³
Example	184	Zinc	0.5	105	A	A	3.21
	185		10	82	A	A	3.21
	186	Zinc oxide	0.5	113	A	A	2.86
	187		3	97	A	A	2.86
	188		10	76	A	A	2.86
	189	Iron	0.7	101	A	A	3.32
	190		3	89	A	A	3.32
	191		10	80	A	A	3.32
	192	Ferrite	0.5	100	A	A	2.86
	193		3	89	A	A	2.86
	194		10	81	A	A	2.86
	195	Stainless steel	0.5	96	A	A	3.32
	196		3	84	A	A	3.32
	197		10	77	A	A	3.32
	198	Brass	0.5	97	A	A	3.39
	199		3	84	A	A	3.39
	200		10	78	A	A	3.39
	201	Lead	5	89	A	A	3.65
	202	Solder alloy	5	92	A	A	3.37
	203	Copper	5	86	A	A	3.45
	204	Nickel	5	86	A	A	3.44
Comparative Example	40	Zinc oxide	0.1	113	A	C	2.94
	41		25	60	C	A	2.94
	42	Iron	0.1	109	A	C	3.32
	43		30	61	C	A	3.32
	44	Ferrite	0.1	105	A	C	2.86
	45		30	62	C	A	2.86

Table 14

Example No.	Resins	Tensile strength, kg/cm^2	Izod impact strength, kg·cm/cm	Flexural Strength, kg/cm^2	Elasti modulus by bending, $x10^4$ kg/cm^2	Molding shrinkage, %		Warping distortion	Moldability	Density, g/cm^3
						MD	TD			
205	66-PA	1590	80	2300	12.1	0.80	0.50	A	A	3.21
206	MXDA	1580	93	2250	12.9	0.71	0.42	A	A	3.21
207	PBT	1200	85	1750	11.1	0.70	0.41	A	A	3.47
208	PET	1620	90	1800	11.2	0.70	0.42	A	A	3.33
209	PC	1490	155	1910	10.9	0.75	0.45	A	A	3.31
210	POM	1410	95	1900	11.9	0.82	0.51	A	A	3.60
211	ABS	1020	110	1500	9.9	0.72	0.44	A	A	3.07
212	PP	690	65	850	5.7	0.89	0.62	A	A	2.80
213	PE	620	50	790	4.9	0.91	0.67	A	A	2.91
214	PVC	650	31	970	10.1	0.85	0.50	A	A	3.52
215	PMMA	710	30	1520	12.9	0.86	0.52	A	A	3.30
216	PI	1280	95	2310	13.9	0.69	0.39	A	A	3.63
217	PSO	1370	92	2010	12.1	0.85	0.55	A	A	3.37
218	PPO	1490	115	1870	10.2	0.77	0.46	A	A	3.08
219	6-PA/PET	1600	88	2050	11.2	0.77	0.48	A	A	3.28
220	6-PA/PPO	1510	97	2000	11.0	0.80	0.49	A	A	3.15
221	6-PA/PBT	1350	87	1970	11.2	0.75	0.45	A	A	3.20
222	PC/PET	1590	111	1860	11.1	0.73	0.43	A	A	3.34
223	PPS	1510	87	2700	21.7	0.51	0.33	A	A	3.83

Examples 224 to 243.

The experimental procedure in each of these Examples was substantially the same as in Examples 145 to 172 except that the molding compositions were each compounded from 10 parts by weight of glass fibers having an aspect ratio of 231 as a fibrous filler, a varied amount indicated in Table 15 below of a powder of zinc (Examples 224 to 233) or zinc oxide (Examples 234 to 243) each having an average particle diameter of about 3 μm as a particulate filler and a varied amount of a thermoplastic resin indicated in Table 15, which also shows the results of the evaluation of the molding compositions.

Table 15

Example No.	Particulate filler, parts by weight	Resin		Tensile strength, kg/cm^2	Izod impact strength, kg·cm/cm	Flexural strength, kg/cm^2	Elastic modulus by bending $\times 10^4$ kg/cm^2	Molding shrinkage, %		Warping distortion	Moldability	Density, g/cm^3
		Kind	Parts by weight					MD	TD			
224	85	6-PA	5	1110	77	1750	13.9	0.70	0.41	A	A	4.99
225	60	6-PA	30	1650	95	2350	10.3	0.85	0.53	A	A	3.80
226	85	PBT	5	850	67	1250	13.1	0.66	0.37	A	A	5.13
227	60	PBT	30	1350	95	1900	9.1	0.75	0.45	A	A	2.85
228	85	PET	5	1210	69	1360	13.2	0.67	0.37	A	A	5.05
229	60	PET	30	1790	99	1950	9.2	0.76	0.45	A	A	2.71
230	85	PPO	5	1100	90	1370	12.2	0.72	0.44	A	A	4.90
231	60	PPO	30	1640	118	2030	8.2	0.81	0.52	A	A	3.53
232	85	PC	5	1090	110	1410	12.9	0.67	0.38	A	A	5.05
233	60	PC	30	1650	165	2060	8.9	0.79	0.48	A	A	2.71
234	85	6-PA	5	1330	97	1930	15.4	0.69	0.40	A	A	4.04
235	60	6-PA	30	1830	115	2550	11.7	0.83	0.52	A	A	2.40
236	85	PBT	5	1050	87	1440	14.6	0.66	0.36	A	A	4.13
237	60	PBT	30	1550	115	2090	10.5	0.74	0.45	A	A	2.60
238	85	PET	5	1400	89	1510	14.6	0.66	0.57	A	A	4.08
239	60	PET	30	1950	119	2140	10.6	0.75	0.43	A	A	2.50
240	85	PPO	5	1290	110	1570	13.6	0.70	0.42	A	A	3.99
241	60	PPO	30	1870	138	2220	9.7	0.80	0.51	A	A	2.28
242	85	PC	5	1290	130	1630	13.4	0.65	0.37	A	A	4.08
243	60	PC	30	1830	190	2230	10.3	0.77	0.46	A	A	4.08

Examples 244 to 251.

The experimental procedure in each of these Examples was substantially the same as in Examples 145 to 172 except that the molding resin compositions were each compounded from 10 parts by weight of glass fibers having an aspect ratio of 231, 70 parts by weight of a zinc powder having an average particle diameter of about 3 µm and 20 parts by weight of a thermoplastic resin indicated in Table 16 below without or with further admixture of 2 parts by weight of the modified polypropylene resin prepared in Preparation Example 1 as a modifier. The fibrous and particulate fillers were used after a surface treatment with 0.5 part by weight of a dimethyl silicone fluid as the water repllent agent. Table 16 below also shows the results of the evaluation of the molding compositions.

Table 16

Example No.	Resin	Modifier	Izod impact strength, kg•cm/cm	Warping distortion	Moldability	Density, g/cm³
244	6-PA	Yes	106	A	A	3.20
245	PBT	Yes	98	A	A	3.46
246	PET	Yes	103	A	A	3.31
247	PPO	Yes	122	A	A	3.06
248	PC	Yes	175	A	A	3.30
249	66-PA	No	97	A	A	3.20
250	12-PA	No	87	A	A	3.00
251	PP	No	69	A	A	2.80

Examples 252 to 261.

The experimental procedure in each of these Examples was substantially the same as in Examples 244 to 251 using the thermoplastic resin indicated in Table 17 below excepting replacement of the zinc powder with the same amount of a zinc oxide powder having an average particle diameter of about 3 μm. Table 17 also shows the results of the evaluation of the molding compositions.

Table 17

Example No.	Resin	Modifier	Izod impact strength, kg•cm/cm	Warping distortion	Moldability	Density, g/cm³
252	6-PA	Yes	117	A	A	2.86
253	PET	Yes	122	A	A	2.94
254	PPO	Yes	137	A	A	2.75
255	PC	Yes	200<	A	A	2.74
256	PET	No	117	A	A	2.94
257	PPO	No	130	A	A	2.75
258	PC	No	200<	A	A	2.74
259	66-PA	No	119	A	A	2.86
260	12-PA	No	98	A	A	2.76
261	PP	No	81	A	A	2.58

Claims

1. A thermoplastic polymeric molding composition which comprises:
(A) from 2 to 70 parts by weight of a thermoplastic polymer as the matrix phase; and
(B) from 98 to 30 parts by weight of a metallic filler, of which the particles have a surface coated with a water repellent agent, the amount of the water repellent agent being in the range from 0.01 to 5% by weight based on the metallic filler before coating therewith.

2. The thermoplastic polymeric molding composition as claimed in claim 1 which further comprises:
(C) a low-molecular oxidized polypropylene in an amount in the range from 0.1 to 2% by weight based on the total amount of the components (A) and (B).

3. A thermoplastic polymeric molding composition which comprises:
(A) from 2 to 70 parts by weight of a thermoplastic polymer as the matrix; and
(B) from 98 to 30 parts by weight of a filler which is a combination of
(B-1) a metallic particulate filler having an average particle diameter in the range from 0.1 to 20 μm, and
(B-2) a fibrous filler having an aspect ratio in the range from 50 to 2500,
in a weight ratio of (B-1):(B-2) in the range from 1:1 to 30:1, the surface of the particles of the component (B-1) and the fibers of the component (B-2) being coated with a water repellent agent in an amount in the range from 0.01 to 5% by weight based on the total amount of the components (B-1) and (B-2) before coating therewith.

4. The thermoplastic polymeric molding composition as claimed in claim 3 which further comprises:
(C) a low-molecular oxidized polypropylene in an amount in the range from 0.1 to 2% by weight based on the total amount of the components (A) and (B).

5. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the thermoplastic polymer is selected from the group consisting of polyamide resins, polypropylenes and poly(butylene terephthalates).

6. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the thermoplastic polymer is selected from the group consisting of polyamide resins, polypropylenes and poly(butylene terephthalates).

7. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the metallic filler as the component (B) is a powder of metallic zinc.

8. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the metallic particulate filler as the component (B-1) is a powder of metallic zinc.

9. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the metallic filler as the component (B) is a powder of zinc oxide.

10. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the metallic particulate filler as the component (B-1) is a powder of zinc oxide.

11. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the fibrous filler as the compo nent (B-2) is selected from the group consisting of glass fibers, carbon fibers, stainless steel fibers, potassium titanate whiskers and aromatic polyamide fibers.

12. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the water repellent agent is selected from the group consisting of silane coupling agents, titanate coupling agents and silicone fluids.

13. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the water repellent agent is selected from the group consisting of silane coupling agents, titanate coupling agents and silicone fluids.

14. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the water repellent agent is selected from the group consisting of 3-aminopropyl triethoxy silane, N-(2-aminoethyl)-3-aminopropyl trimethoxy silane, isopropyl triisostearoyl titanate, isopropyl tri(N-aminoethyl aminoethyl) titanate, dimethyl silicone fluids and methyl hydrogen polysiloxanes.

15. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the water repellent agent is selected from the group consisting of 3-aminopropyl triethoxy silane, N-(2-aminoethyl)-3-aminopropyl trimethoxy silane, isopropyl triisostearoyl titanate, isopropyl tri(n-amidoethyl aminoethyl) titanate, dimethyl silicone fluids and methyl hydrogen polysiloxanes.

16. The thermoplastic polymeric molding composition as claimed in claim 2 wherein the low-molecular oxidized polypropylene as the component (C) has an average molecular weight in the range from 1500 to 20000.

17. The thermoplastic polymeric molding composition as claimed in claim 4 wherein the low-molecular oxidized polypropylene as the component (C) has an average molecular weight in the range from 1500 to 20000.

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(54) A thermoplastic resin-based molding composition.

(57) The thermoplastic polymeric molding composition of the invention has good moldability in shaping by injection molding, extrusion molding and compression molding and capable of giving shaped articles having good machinability in mechanical working such as cutting, grinding and lathing. The composition is compounded from 2 to 70 parts by weight of a thermoplastic polymer such as a polyamide resin and from 98 to 30 parts by weight of a metallic filler such as zinc powder and zinc oxide powder having a surface coated with a water repellent agent such as silane coupling agents, titanate coupling agents and silicone fluids in a specified amount. A part of the above mentioned particulate filler may optionally be replaced with a fibrous filler such as glass fibers and carbon fibers so that the shaped articles of the molding composition may be imparted with increased impact strength.

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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 769 260 (L. SEGAL) * Claims; column 4, line 45 - column 5, line 33; column 6, lines 20-30 * ---	1-6,11-13	C 08 K 9/04 C 08 K 9/06 C 08 K 3/08 C 08 K 3/22
P,X	CHEMICAL ABSTRACTS, vol. 107, no. 24, 14th December 1987, page 44, abstract no. 218680w, Columbus, Ohio, US; & JP-A-62 79 259 (SEIKO EPSON CORP.) 11-04-1987 * Abstract * ---	3,6,11,13,15	
X	GB-A-2 117 410 (MITSUBISHI PETROCHEMICAL CO. LTD) * Claims * -----	1,5,7,12,14	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 08 K
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-10-1989	DE LOS ARCOS Y VELAZQUEZ

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